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BIOFUELS FOR TRANSPORT IN THE 21st CENTURY: WHY FIRE SAFETY IS A REAL ISSUE

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ABSTRACT

Years after pioneering development of sugar cane ethanol in Brazil (started in the mid 70's), with the new century venue we are assisting of a booming industry regarding biofuels for transportation in general, at international level. However, fire safety has not appeared so far as a potential bottleneck for future sustainable development, nor has it been anticipated that fire safety misleading judgements or lack of safety management might act as a non technical barrier for sustainable development.
This paper is a first contribution to discuss these issues within the fire safety community aiming at identifying research needs and bring a first overview based on life cycle and whole value chain perspectives of biofuels for transport. This contribution is a first output from a National research program named BIOSAFUEL piloted by INERIS, comprising a first analysis of fire risk typology presented by so-called in Europe 1st generation technologies of biofuels. When the first statement is to consider that fire safety aspects are not likely to be that much critical on a technical point of view, the analysis is showing that safety related issues –and more especially fire safety related issues– with biofuels are not correctly summarized by simply saying that fuel ethanol is a flammable product whereas biodiesel is not, from a regulatory point of view. A more in-depth analysis is needed, that will, in addition, have to consider significant changes in biofuel technologies in the future.

INTRODUCTION

Nobody from both sides of the Atlantic Ocean can ignore by now what biofuels are and represent in terms of alternative fuels for the automotive sector, considering nearly daily media reporting regarding that tremendous activity actively. Indeed, biofuels had a long and chaotic history in the past, the development of which was more or less killed by the dominance of the cheap oil era. However, say since the 2000's, a new phase, that everyone hopes sustainable, is currently supported by a number of key drivers. These key drivers vary slightly from country to country, most common being:

- using biofuels secure or diversify fuel supplies (USA, Western Europe...)
- biofuels are assumed to have very limited –if any– impact on global climate change (CO_2 emissions are compensated by photosynthesis at level of the growing biomass) and induce, as oxygenates, improved combustion properties limiting pollutant emissions
- biofuels offer opportunities for developing or diversifying rural economy (source of employment)
- tax incentives or other financial supports for farmers, biofuels producers, or users
- other policy driven regulatory frameworks (ex. clean fuel act in the USA, Directive 2003/30/CE in the EU...)

In addition, regular sharp increases in oil prices are reminding to western countries associated geopolitical issues of fossil fuels reserves and ineluctable diminution of relating ressources (have we passed through the so-called oil peak ?).

Consequently, a tremendous research effort to develop and improve biofuels production and use has been implemented for years, however, very limited consideration of safety issues has been given so far (apart from material compatibility issues at the level of vehicles). Aren't there any real new challenges regarding safety, and fire safety in particular ? At time France is going a step forward in boosting the use of biofuels on the National market, INERIS has been granted to produce a first overview of the question. This is in the scope of a three years research project called BIOSAFUEL®[1,2] started in January 2006.

GENERAL FACTS AND FIGURES ABOUT AUTOMOTIVE BIOFUELS

The conventional biofuels, namely fuel ethanol or biodiesel, both derived from energy crops (sugar containing and starch containing plants, or oil seeds, respectively) have reached an industrial development in Brazil, in the USA, and in a few countries in Europe for at least two decades or more, whereas big expectations are anticipated for the new routes of production of biofuels under development from biomass (lignocellulosic resources). Given the vast availability of that renewable resource, the current debate that raises potential conflicts such "fuel versus food ? " or the risk of biodiversity would no longer exist when such production routes will be commercially available. The readers may refer to a number of very recent books to appraise how far is the interest of the scientific community for the global biofuels activity and related market[9,10,11,12,13]. The tremendous number of conferences dedicated to biofuels issues is also very impressive, as largely revealed by a brief web search or by reading dedicated newsletters of journals [Licht reports on ethanol and biofuels][IEA task 39 newsletters].

Table 1: top 5 producers of ethanol
Data 2005, Source: C. Berg (after ref. [3])

Countries	*Production (millions liters)*
Brazil	16,500
USA	16,230
China	2,000
E.U.	950
India	300

Table 2: top 5 producers of biodiesel
Data 2005, Source: F.O. Licht (after ref.[3])

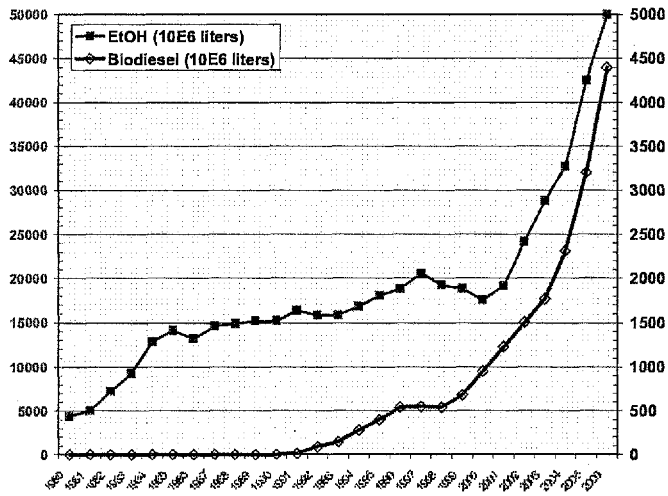
Countries	*Production (millions liters)*
Germany	1,920
France	511
USA	290
Italy	227
Austria	83

Table 3: biofuels profiles of selected countries (from ref.[4])

Country	**Production (2005 liters)**		**Leading feedstocks**		**Recent enabling legislation/ body**	**Blend mandates/goals?**	**Remarks**
	Ethanol	**Biodiesel**	**Ethanol**	**Biodiesel**			
United States	15B	290M*	Corn	Soybeans	Energy Policy Act of 2005, VEETC	Yes (28.35B liters by 2012)	National energy security large motivator for biofuel programmes; subsidy of 51 ¢ per gallon of ethanol used in fuel and a 50 ¢ or $1-a-gallons subsidy for biodiesel; many subsidies at state level as well.
European Union	950M*	2.3B (2004)	Cereals and sugar beets	Rapeseed	Directive 2003/30/EC	Yes (2% by 2005 (not met) and 5.75% by 2010)	Policy goals: mitigate climate change, secure energy supply, advance technology, and diversify agriculture; land scarcity makes blending goals difficult without imports; tax concessions for bio-energy.
Brazil	16B		Sugarcane	Castorbean oil, soya oil	PROALCOOL (1975) & National Biodiesel Programme (2002)	Yes (20-25% ethanol, 2% biodiesel, 5% in 2013)	World's largest ethanol producer and exporter; produces ethanol at lowest cost; well developed biofuel transportation infrastructure; biodiesel "H-Bio" recently developed and patented by Petrobras.
Guatemala	64M****		Molasses	Jatropha		No	Excellent sugar cultivation; investigated by EU for dumping ethanol; Brazilian investors are investing in distilleries and hope to create market for flexfuel cars.
China	3.6B		Maize, cassava, rice	Waste cooking oil, vegetable oils	Renewable Energy Law of the PRC (2005)	Yes (in certain provinces)	Vehicle ownership increased 600% in last decade driving fuel demand** and the need for alternative fuels; China's policy on biofuels will largely determine the development of biofuels on a global scale; incentive programmes for ethanol.

(courtesy UNCTAD secretariat)

Quantities of biofuels put on the market drastically increased in recent years, as indicated in figure 1. This sharp increase translates the emergence of a real world market for biofuels, with current major actors being mentioned in tables 1 and 2. It is worth to notice that the USA will have overturned Brazilian production of bioethanol in 2006 for the first time, as a result of promotion policies at both State and Federal levels that resulted in many new plants for processing bioethanol from corn. It must also be outlined that many emergent countries, generally located in the tropical area are involving themselves in the biofuel industry due to climate opportunities (for example for producing palm oil and derived biodiesel). China, dramatically lacking fossil oil, and India are also becoming, as can be seen, major actors on the fuel ethanol side. Table 3 complete general information on the biofuel market indicating the current context in a selection of countries.



NB. : 2005 & 2006 are estimates

Figure 1: history of production of fuel ethanol and biodiesel from the early 1980's up to 2006-12-21 adapted from ref.[3]

Classification of biofuels

There is no unique classification of biofuels accepted at international level. There are currently basically two major types of fuels, corresponding to current major industrial pools of fossil liquid fuels: bioethanol, which may be blended in various proportions with unleaded gasoline for use in gasoline fuelled cars or in so-called flexfuel vehicles, and biodiesel, which can be blended with diesel for use in diesel cars. In this paper, we focus on liquid biofuels, representing the vast majority of currently commercialized biofuels. In his final report[5], regarding the elaboration of a research agenda for biofuels in the European Union, the BIOFRAC proposed the following conventional classification scheme (see table 4 and 5) for biofuels of current and future interest for the automotive transport.

Table 4: biofuels of first generation : adapted from ref. [5]

Biofuel type	Specific name	Biomass feedstock	Production process
Bioethanol		Sugar beet, sugar cane, grains (corn, wheat, barley), potatoes, ...	Hydrolysis and fermentation
Vegetable oil	Pure Plant Oil (PPO), also called Straight Vegetable Oil (SVO) elsewhere	Oil crops (e.g. rape seed, sunflower seed...)	Clod pressing/extraction
Biodiesel	Biodiesel from energy crops Rape seed methyl ester (RME), fatty acid methyl /ethyl ester (FAME/FAEE)	Oil crops (e.g. rape seed, sunflower seed...)	Cold pressing/extraction & transesterification
Biodiesel	Biodiesel from waste FAME/FAEE	Waste/cooking/frying oil/animal fat	(optional) pretreatment & transesterification
Biogas	Upgraded biogas	(wet) biomass	Digestion and refining
Bio-ETBE[1]		Bioethanol (etherified)	Chemical synthesis

Note: [1]:Ethyl Tert Butyl Ether

Naturally, biogas, obtained from wet biomass residues, is also a reality, but is of limited, and generally local, use. Safety issues are naturally pertaining also to such a gaseous fuel: the fire risk is present, as with all other flammable gases. Moreover, a dramatic accident at the process level that took place recently in Germany reminded us also of potential toxicity related issues with biofuels[6].

Table 5: biofuels of second generation : adapted from ref.[5]

Biofuel type	Specific name	Biomass feedstock	Production process
Bioethanol	Cellulosic bioethanol	Lignocellulosic biomass (ex. wheat straw, corn stroves...)	Advanced chemical and/or enzymatic hydrolysis and fermentation
Synthetic biofuels	Biomass to Liquid (BtL): Fischer Tropsch (FT) diesel, Synthetic biodiesel, biomethanol; heavier mixed alcohols, biodimethylether (DME)	Lignocellulosic biomass	Gazification, gas shift and synthesis
Biodiesel	Hydrotreated biodiesel (ex. : Next-BtL process)	Vegetable oils and animal fat	Hydrotreatment
Biogas	SNG (Synthetic Natural Gas)	Lignocellulosic material	Gazification & synthesis or biological process

Fire safety general considerations

At evidence, fire safety considerations pertaining to the biofuels industry must take into account:: a) safety data of the concerned products; b) safety data of the whole list of substances that may intervene on the whole value chain if we want to evaluate safety issues with a life cycle analysis perspective; c) process safety consideration; d) organizational aspects; e) storage and transport issues; f) any other related pertinent topics.

As an example of the latter point, and not necessarily easily perceived, the analysis of fire safety issues must take into account differences that are pertaining to local conditions of development and use. Fire safety experience accumulated so far by the biofuels industry (and very poorly valorized in the open literature in our view) is not necessarily directly transferable from one place to another, due to differences in production technologies, environmental constraints and many technical details, including significant differences in safety culture.

As an example, Brazil has accumulated some 30 years of experience with the production and use of sugar cane ethanol and has implemented by now some 30,000 stations delivering 100% ethanol (hydrated) and gasoline/anhydrous ethanol blends up to 25% rich in ethanol. The extensive use of dedicated vehicles using hydrated ethanol is a unique experience in Brazil. Moreover, Brazilian model of FFV (Flex-fuel vehicles) that has now reached a commercial status since 2003 in replacement to dedicated vehicles for the use of hydrated pure ethanol is simply not applicable in Europe, due to the presence of a secondary fuel tank installed in the engine compartment (see fig. 2). In addition, Brazil recently announced brand new plans for developing biodiesel micro-units and related use for developing rural economy, as well as a long term plan for ethanol aiming at weighing some 10% of the world market in 2025, inducing many technical modifications at many levels of the life cycle of ethanol (sugar cane production and pretreatment, bioethanol processing, technical schemes for exports...).

By contrast, elsewhere (USA, Europe...) the development of E85 as an alternative fuel has been chosen – in addition to ethanol/gasoline blends with low concentrations in ethanol (E5, E10). The (modern) FFV vehicles delivered in the USA and in Europe are designed to be able to work with any ethanol/gasoline mixture with up to 85% in ethanol, but the experience with distribution networks for E85 keeps so far very limited (some 300 refuel stations available in Sweden, which looks impressive for such a small country, but only 49 refuel E85 stations available for all US States of America, for a corresponding vehicles fleet capable of using it of 30000 in 1999, according to ref.[7]).

In the USA by contrast, the development is more piloted by the need to secure fuels supply, and an ambitious expansion plan of biofuels production has been suggested (in particular from the promising route involving cellulose ethanol): Developing cellulose ethanol at industrial scale is currently perceived by US politicians as a good part of the solution. To finalize this idea that local considerations are of importance, let us report on recent moves in France and Belgium.

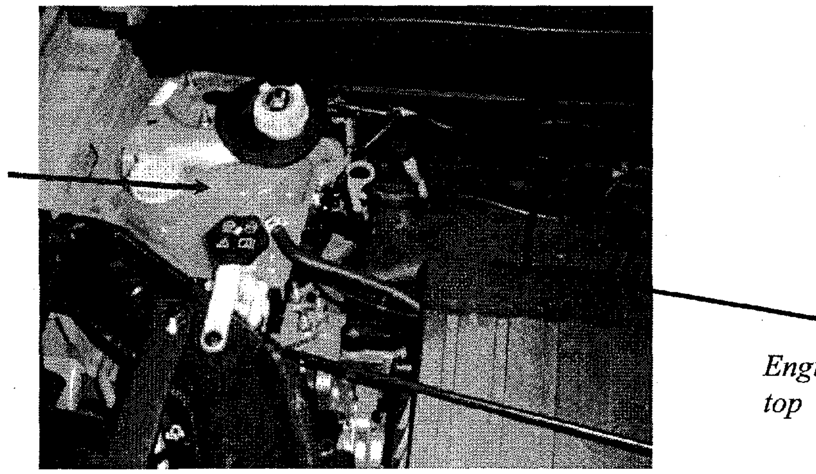


Figure 2: auxiliary gasoline fuel tank (E25) located in engine compartment of a typical Brazilian Flex-fuel car

France has pioneered the industrial production of biodiesel from vegetable oil by homogenous catalysis transesterification (first unit operating since 1992 in Compiègne), and has started to use fuel ethanol in diluted blends for some ten/fifteen years. France keeps one of the leaders, at European level, for biofuel production (rape seed methyl ester in particular), however, no specific distribution network for delivering biofuels is currently existing: France, for a number of reasons, has opted so far to limited (and not registered at the pump) incorporation of biodiesel in the diesel pool and of bio-ETBE (the ether derived from sugar beet ethanol by synthesis with isobutene) in the gasoline pool. But the French Government officially announced the promotion of an E85 network in last September, and official authorization of this new fuel by 1st January 2007, with the ambition of implementing some 500 E85 dispensing stations by 2008. Belgium, on his side was until recently far below the objective fixed by the EU in 2005 (as many European countries) but has by now started internal production. Some 5/8 projects are currently under development (or in construction) to procure a reasonable production capacity which will have to be completed by imports. Safety issues relating to storage and transport (notably by water streams) are likely to be there of major importance for such a heavily densely inhabited country.

BIOFUELS TECHNICAL DATA IN RELATION WITH THE FIRE PROBLEM

Table 6 presents important data regarding fuel ethanol and related gasoline/ethanol blends constituents. MTBE (Methyl Tert Butyl Ether), also mentioned, has been banned in 18 States of USA. This situation is at the origin of the initial promotion of ethanol as an octane enhancer (anti-knock) substance as a substitute. Butanol data are also provided, as sometimes considered as a potential alternative fuel presenting some advantages compared to ethanol (such as a heating value closer to gasoline). However, the general view is that butanol from fermentation of biomass is not yet competitive. Some recent projects however are reactivating the interest of butanol[8].Table 7 gives similar data for biodiesel (fatty acid methyl or ethyl esters of vegetable oils).

Table 6: safety characteristic data of major products involved in bioethanol production

N.B.: figures from various sources, such as ref.9 to 13 or MSDS; (a) estimates from ref.14

Products	Vapor Pressure (kPa)	Boiling point (°C)	Flash point (°C)	AIT (°C)	Density (20°C) (g/cm^3)	LEL-UEL (% air)	LHV (MJ/kg)
Ethanol	5.8 (20°C) 15.9 (37.8°C) 29.4 (50°C) 15.9 (38°C)	78.4 78	12 13	363-425 400 423	0.79 0.794 (15°C)	3.3-19 3.1-27.7 4.3-19 3-19	26.8 26.8
ETBE	21 (25°C)	73	-19	~310	0.75	1.2-9.1	35.9 36.3$^{(a)}$
MTBE	27 (20°C) 33 (25°C)	55.3	-28	224-460	0.746	1.5-8.4	35.2 35.9$^{(a)}$
Butanol	0.67 (20°C)	118	35	340	0.81	1.4-11.3	36.1$^{(a)}$
Methanol	3.8 (0°C) 12.3 (20°C) 34.4 (40°C)	65	12 11	464 455	0.791	5.5-31	19.9
E85	38-83 (38°C) 41-83	35.5-76.7 49-80	-45-10 slightly higher than gasoline	257.2 > gasoline	0.78-0.79 (15°C)	1.4-19 between ethanol and gasoline	22.4-22.9
Gasoline	48-103 (38°C) 50-100	30-190 27-225	-40 -43	257	0.73-0.76 0.69-0.79 (15°C)	0.6-8.6 1.4-7.6 1-8	42.9 43.2

LEL-UEL : Lower explosion limit -Upper explosion limit (vary according to ref. temperature)

Table 6 essentially illustrates basic flammability parameters of ethanol, showing in particular that flammability is a real issue that differs from the gasoline case. Whereas from table 7, it can be stated that biodiesel is a fuel reasonably comparable with conventional diesel in terms of fire risks, in a first glance. However, the fire risk is much more complex with ethanol that the simple expanded flammability range (on the reach side) that appears from the data in table 6.

Table 7: safety characteristic data of products involved in biodiesel production

N.B.: figures from various sources, such as ref.9 to 13 or MSDS; (*): value for FAME

Products	Viscosity (40°C) (mm^2/s)	Boiling point (°C)	Flash point (°C)	AIT (°C)	Density (20°C) (g/cm^3)	LEL-UEL (% air)	LHV (MJ/kg)
Rapeseed Oil	30.2	n.a.	300-324 > 320°C	n.a.	0.92	n.a.	39.7 (HHV)
RME	4.5 4.83 4.46	170-366 320-350	170-180 153-179 179	n.a.	0.88 0.883 (15°C)	n.a.	37.4$^{(*)}$ 42
FAEE	6.17	358	185 175-185	n.a.	0.876 (15°C)	n.a.	40
Diesel	2-4.5	160-350 188-343	70 74	316	0.82-0.86 0.82-0.845 (15°C)	1-6	42.6 42.9
FT diesel (synthetic)	2.4	211-297.7	95.5	n.a.	0.77 (15°C)	n.a.	~43

The global fire risk with the end use product must take account of the following additional considerations: a) although moderately volatile (relatively high boiling temperature and heat of vaporization 2.5 higher than for gasoline), ethanol in blends with gasoline, has the capacity of forming low boiling azeotropes with gasoline components of low molecular weight that leads to critical volatility issues with the blends, b) electrical conductivity is 35,000 times higher than for gasoline, c) ethanol is a polar solvent, and as such requires special fire-fighting procedures to tackle significant fires, d) the product present significant corrosivity (to metals and plastics), e) ethanol is hydroscopic, fully miscible with water, but in blends with gasoline and traces of water, demixtion problems exist (e.g. phase separation may occur, depending on concentrations of the three components): this is particularly important with blends with low ethanol contents.

Some of those properties are implementing indirect fire risks at level of storage of ethanol blends, and end-use of ethanol blends in cars, due to potential leakage through material attack by corrosion. The question of the right selection and location of flame arresters in cars and in refueling stations for the use of E85 is still an open question, as shown by some recent work[15, 16]. Limited experience of E85 distribution networks at the EU level currently justifies careful examination of these issues in France, as well as in the USA[17].

Naturally, considering the full life cycle of biofuels, this section would gain benefit through pertinent data acquisition regarding other materials and chemicals intervening in the life cycle of biofuels. As an example, some 10 chemicals (including gasoline) are in the list of potential ethanol fuel denaturant in Europe, distillation residues like fusel oils, of important value, also present fire risks due to flammability properties. The list of potential catalysts in use or currently tested for biodiesel production is still much higher. Products in use for odour reduction, maintenance purposes, or alcohol rectification or other treatment (desulfurization using potassium permanganate), or fuel additives (like anti-oxidizers) are other families of chemicals that deserve interest from the fire safety point of view. One major problem to look further on these compounds is bound to the fact that many of them are proprietary.

AN ANALYSIS OF THE TYPOLOGY OF THE FIRE RISK BY BIOFUELS FROM AGRO-RESSOURCES SUPPLY TO END USE AND RELATED ACTIVITY

Bioethanol life cycle analysis and the fire risk issue

From a life cycle perspective, the fire safety engineer may need to consider ethanol processing as well as side aspects that may play significant roles as well, such as conditions of feedstock supply, storage, handling and pre-treatment, import and export issues, management of by or co-products that differ according to biomass feedstock under consideration. Some of the feedstock are directly releasing sugars or sugar based co-products like molasses, that are directly fermentable by use of micro-organisms (generally yeasts) into ethanol (e.g. sugar beets or sugar cane). Starch containing crops, like potatoes, wheat or corn, require more sophisticated break-down of the feedstock, by processes that may involve cooking and adding enzymes. Although processes thus vary from one case to the other, the core of the fuel ethanol process remains based on same basic chemical processes (or biological processes) like hydrolysis (acidic, enzymatic or combined), saccharification (optional), fermentation, distillation, refining and rectification (such as P and S removing, or denaturant addition).

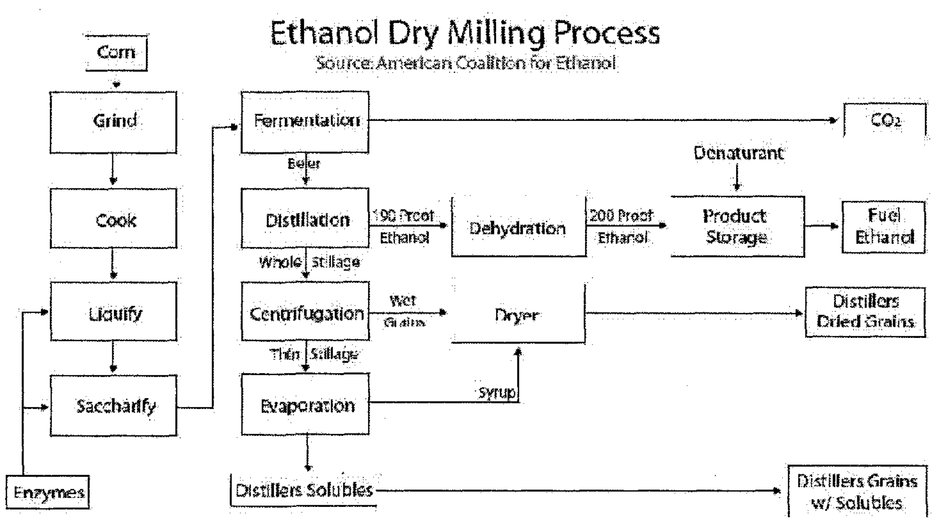


Figure 3: insight on the most common fuel ethanol process from grains (corn) in the US

In those processes, the risk pattern is very closely related with conventional edible alcohol or industrial distilleries, at least at the process level, which suggests that major achievements terms of fire risk management with those other ethyl alcohol uses might be helpful for assisting the development of the biofuel industry. The treatment of co-products, for use in the animal feed (plant residues) or for other purposes (fusel oil components valorization) may be more specific. Let us add as well the dehydration step, required for fuel ethanol in most vehicles capable of running with ethanol/gasoline blends for a number of reasons. Vapour is used to do this final step, a source of significant heat.

As an example, Figure 3 summarizes the main steps of bioethanol processing from corn, referring to the so-called dry milling process, the most popular one in the USA today, for reasons of limited investment costs. The analysis of the flowsheet helps in identifying potential fire risks, like:

- self heating of raw material or derived crushed products (during corn mashing)
- creation of explosive atmospheres (vapour or dust) and related explosion risk in tanks
- fire risk induced from excessive heat transfer to products due to malfunctioning of handling systems or cookers (treated feedstock) or dryers to products (co-processing of by-products to obtained dried distiller grains...)
- operational problems on the distillation process (see for instance paper from Kvaalen[19])
- use and storage issues of various flammable products
- use of other dangerous substances (acids, bases)
- storage of gas (CO_2) under pressure.

Those risks are quite conventional and relatively well known, but they are real issues, more or less well addressed according to regulation background and existing safety culture. One should also be very cautious of the analysis of consequences of requested flexibility of an ethanol process plant in terms of : a) various grades of feedstock that will have to be treated, b) various options defined for the valorization of co-products, as the type and form of "in" and "off" substances will clearly influence pertinence of storage and handling equipment and procedures, in terms of safety management. Naturally, the way fuel ethanol is introduced after production in the gasoline pool (transportation issues: road, rail, pipelines...), blending issues, ethanol/gasoline dispensing stations safety equipment, equipment compatibility for storage and at level of the car manufacturers are typical specific issues that deserve interest of the scientists.

Going further on the end use side, it must be noted that ethanol could also be considered in the future as a candidate for use as a component in blends with diesel, and why not biodiesel:

- the US DoE has carried out a testing program in the area for about 10 years, for a potential use on heavy duty engines;
- there is also a special interest in Europe like in France or Germany, countries in short of diesel and too large in gasoline, for technical reasons (existing refineries configurations and local consumers attraction for diesel cars).

However, with ethanol/diesel blends (so called E-diesel or bioE-diesel), many challenges are still existing[18], including in relation with fire safety (stability of the mixtures, protection of car tanks and fuel distribution line to the engine...).

In the future, other technical challenges pertaining to the fuel bioethanol industry that will also interact with fire safety management will also entail the development of new routes of production, more integration of biofuel production into biorefinery concepts (where the full valorization of the energy crop or the biomass feedstock will be the global objective) or even the use of ethanol as a source for biohydrogen processing.

Biodiesel life cycle analysis and the fire risk issue

There also, addressing properly the fire issue globally, starts by considering much more input than the limited combustibility properties of vegetable oils or fats (the needed material to process biodiesel by chemical three steps reaction called transesterification (see figure 4)) and the biodiesel by itself.

Quick examination of the main reaction process (figure 4) and the global process flowsheet (figure 5) reveals why flammability is also a key issue: the fire danger may arise at least from two major products intervening in the chemical process:

- the main reactant in the chemical reaction that converts the triglycerides into fatty acid alkyl esters: most of the time methanol is chosen, giving the conversion of the oil into fatty acid methyl esters or FAME (see table 6 for methanol flammability properties),
- and the catalyst generally necessary to reach satisfactory conversion rate or conversion time duration. Catalysts may be selected in the following family list[9] : a) alkali metal hydroxides or methylates, alkali metal or transition metal soaps, alkylguanidines b) acid catalysts (mineral acids, sulfonic acid, ion exchange resins, zeolites c) others like titane alcoholates, diverse metal oxides.

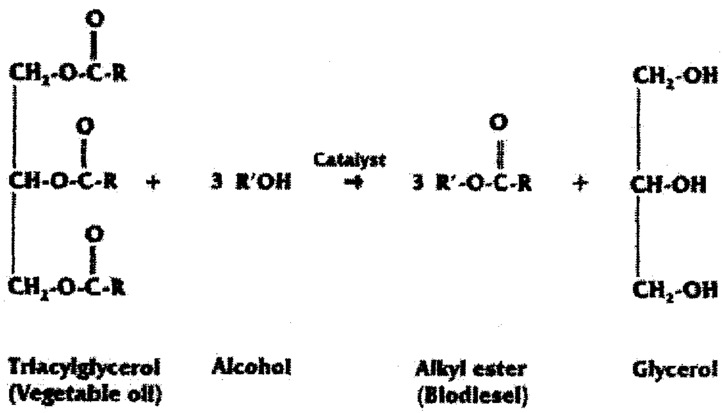


Figure 4: the chemical reaction of transesterification

As can be seen, a number of dangerous materials is involved in the sole reaction at the core of biodiesel production, notwithstanding other materials in used in other parts of the biodiesel life cycle.

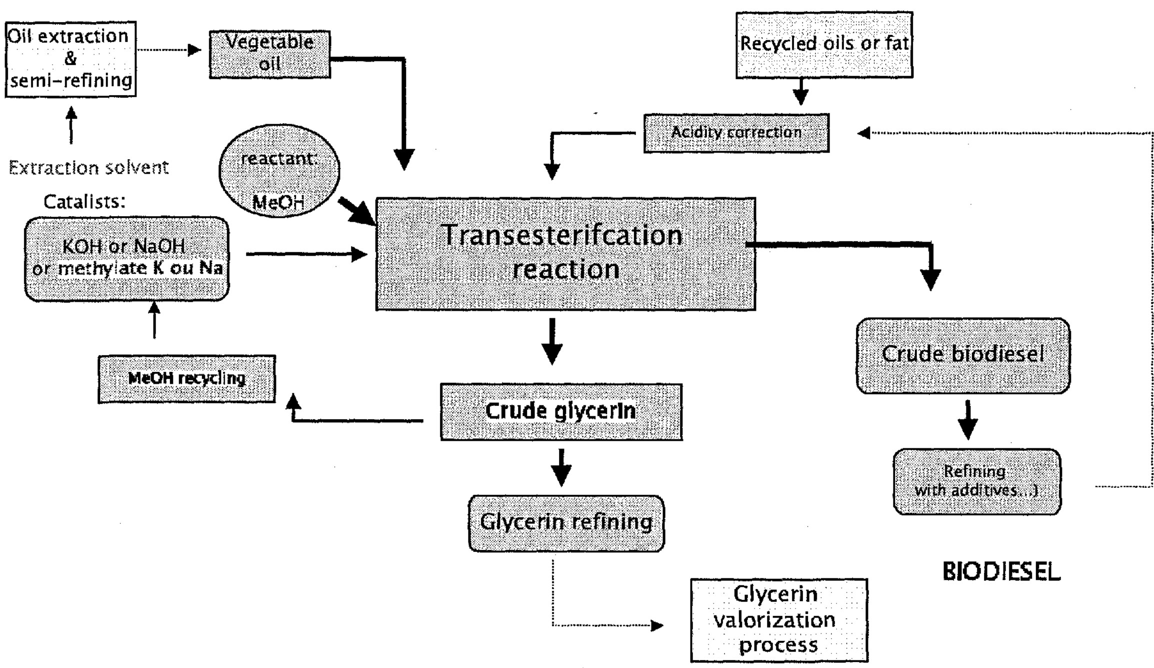


Figure 5: general flowsheet for biodiesel processing using homogeneous catalysis

Sodium or Potassium methylates, the most commonly used catalysts with sodium hydroxide present the particularity of being solid at normal temperature and pressure. Dissolution of the methylate powder in methanol is then a key "dangerous" step in the process, as it leads to potentially highly exothermic reaction and gives rise, in the same time of a potentially explosive composite (vapor + dust) atmosphere. Such an operation generally requires adapted preventive measures[20]. Apart from the transesterification process, figure 5 also reveals other potential fire related risks, regarding methanol recovery from the crude glycerin tank, pre-esterification steps by use of acids, or refining processes of both glycerin and crude biodiesel that may require distillation phases. Oil seed processing, that can be done in biodiesel plants or in specialized oil refineries, also present special fire risks, such as the use of n-hexane as for complementary solvent extraction from seed cakes after screw extraction. The next section which essentially provides two lists of significant incidents, classified by type of biofuels, is a consolidation of our analysis.

A REVIEW OF RECENT INCIDENTS

Tables 8 and 9 present a selection of recent accidents of particular interest to consolidate our analysis. A Word of caution is needed however.

Table 8: incidents relating to bioethanol fuel industry that occurred in the 2000's

N.B.: figures from various sources, such as ref.21 and many press releases

#	Date & location	Known facts about the incident	consequences
1	21/03/2000, South Bend (USA)	Fire initiated and contained in a bag-house filter, collecting dust from corn drying process. Fire extinguished by fire brigades in 30 min.	No injury, $20,000 damage
2	14/09/2002, Atchison, KA (USA)	Blast in a distillation plant (wet milling process), followed by alcohol tank fire. Hopefully, major alcohol tank farm was separated from the process plant area	4 workers injured
3	22/10/2003, Benson, Minn. (USA)	Massive Explosion of a 40,000 gal. Of corn mash, may be additional explosions. Parts of the tank flew away, one hitting a tank truck getting loaded with fuel ethanol, 75 feet away, another dropped through roof of an adjacent processing room	1 killed, 1 injured
4	26/07/2003, St Paul, Minn. (USA)	An odor-reduction equipment (thermal oxidizer) overheating caused a fire in the insulation of the roofing materials. 3rd fire reported at this plant…	1 fire-fighter injured; $15,000 damage estimate
5	28/01/2004, Port Kembla, (Australia)	Major ethanol tank fire (4,000,000 liters) in a petroleum terminal, after initial explosion that blew away the 5 tons tank roof. Fire-fighting operations made difficult due to polarity of EtOH, damage on plastic part s of cars up to 50 m away. Fire put out after more than 20 hours using alcohol resistant foam drops by helicopter.	2 injured
6	29/02/2004, near Porthmouth, VA (USA)	On its way from NY to Houston, the Bow Mariner, a 3.5 mln gallons Ethanol tanker exploded and sank 50 miles off the coast	21 crew out of 27 members killed or lost
7	16/05/2005, Groton, SD (USA)	Fire at the ethanol process plant, handled up to arrival of fire-brigades by the facility sprinkler system. Fire reported due to equipment malfunction	No injury; minor damage
8	22/09/2005, West Berlington, Iowa (USA)	Fire at level of a dryer (for the production of DDGs) at a 40,000 gal ethanol dry milling unit	2 people suffered minor injuries
9	15/02/2006, Lillers, (France)	Fire declared in a sugar producing &distillery complex, outside of the ethanol tanks farm, at level of a denaturant storage unit. The fire is reportedly due to electrical malfunction of the heating system	No injury; Existing Containment basin limited fire spread
10	22/05/2006, New Hemburg, (USA)	Fire on board of tugboat the "Pacific Reliance", pushing a barge full of ethanol, on its way to Baltimore by the Hudson River: fire was in the engine compartment and was put out within 20 minutes	No injury nor pollution
11	15/06/2006, Shively KY (USA)	Very short flash fire at an ethanol plant, during routine maintenance work (replacement of old pipe at filling station area of the facility)	2 people treated for burns
12	20/10/2006, New Brighton, PEN, (USA)[22]	On its way from Chicago to New Jersey, A freight train derailed over a bridge, not far from Pittsburgh. The train was conveying some 85 tank cars of ethanol, 24 of them were involved in the derailment over the Beaver River; 9 of them turned into explosion & fire scenario	No one injured, significant damage with rolling stock, river pollution

No statistical analysis of the level of risk shall be driven from those tables in order to rank biofuel producers (in terms of companies or even countries): for example, the absence of any incident originating from Brazil (the leading country in fuel ethanol production and use until 2005!) simply translates the difficulty to get appropriate information in existing database, as it is more that likely that accidents have and may be still do happen sometime.

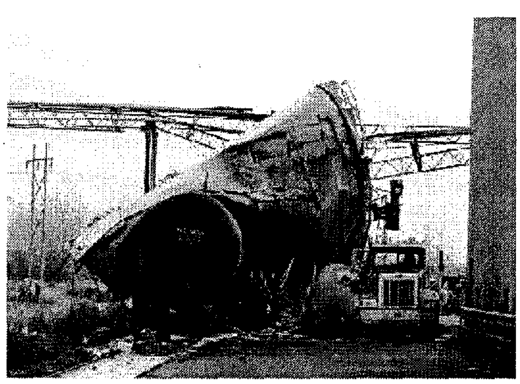
Although considerable experience was existing with ethanol distillation before the emergence of the fuel ethanol market and although biodiesel is hardly ignitable, the careful examination of data in table 8 and 9 clearly shows that both alternative fuels have suffered significant incidents considering their life cycle and also illustrates the wide variety of scenarios. Owing to the flammable character of ethanol, it is not surprising to see that explosion and fire scenarios involving ethanol fuel stocks have indeed occurred in some of the incidents recorded in table 8, either as the initial event, or as a "domino" effect. One may also see that incidents are material related or equipment related or both.
The well known Port Kembla tank fire (#5 in table 8) presents some similarities with a former ethanol tank blaze that happened in the Netherland on the 18 February 1998 in Bergen op Zoom[23]. Those two scenarios have clearly illustrated that emergency response to be given to fuels tanks added with significant amounts of ethanol deserve special considerations. As a matter of fact, a modification of the UN recommendations for Transport of Dangerous Goods (the so-called "Orange Book") has just been adopted end of 2006, that creates a new UN number to identify fuel blends containing more than 10% of ethanol, to facilitate adequate emergency response plans in case of a fire.

Table 9: incidents in relation with the biodiesel industry

N.B.: figures from various sources, such as ref.21 and many press releases

#	Date & location	Known facts about the incident	Consequences
1	04/08/2003, Grand-Couronne, (France)	Fire declared in a cooling tower, associated to biodiesel processing plant	No injury; unknown damage
2	11/01/2006, Brussel Ring, (Belgium)	Multiple car crashes after sunflower oil leak from tank truck on motorway close to airport. No fire but very difficult cleaning procedure due to frost	Major traffic disruption or congestion
3	17/02/2006, Bakersfield, CA (USA)	A biodiesel recent plant suffered a violent fire during several hours, as a result of a outside methanol fire that spread into the process plant. Ignition of methanol occurred due to leakage (electrostatic discharge ?)	Total loss of the refinery; No injury
4	07/05/2006, residential area, Colorado (USA)	Tank of homemade biodiesel left unattended caught a fire due to overheating of heating device. Destruction of shed and surrounding equipment	Local damage
5	23/06/2006, Canby, OR (USA)	Major fire involving canola biodiesel stock erupted at small biodiesel processing site. Difficult fire fighting.	Significant damage
6	07/07/2006, New Plymouth, ID (USA)	An explosion occurred, followed by a fire, in a brand new biodiesel small plant. The explosion is consecutive of unsafe welding operation above a glycerin tank under refining process	1 worker killed by the explosion; significant damage
7	17/7/2006, Venette, (France)	Banal "chimney fire" at the historic first biodiesel production unit in France. Some related "societal acceptance" issues.	Very limited due to prompt reaction

Figure 6: domino effect consecutive of Benson incident in Minnesota



(see incident #3 in table 8)

Figure 7: the impressive rail transport incident in Pennsylvania

(see incident # 12 in table 8)

Among the lessons learnt from the listed incidents is the significance of the risk during transports. Massive transports of vegetable oil and fuel ethanol, by road, rail and maritime routes is likely to occur in the future, and those incidents, even not necessarily followed by a fire (a number of recent train derailment or tank truck overturns had occurred without consecutive fire incidents in a reported number of cases in North America[21] before the occurrence of incident #12 in table 8), are potential events that require emergency preparedness. Table 9 listing of incidents regarding biodiesel clearly illustrates that the fire risk with biodiesel may be linked with the product itself, and to flammability issues of other materials used to process it like methanol or mixtures of glycerine and methanol. At last, Biodiesel processing is increasingly popular as a "hobby" at home: a situation that recently led the Health and Safety Executive to address a safety warning on their web site[24] : low cost batch reactors can be supplied from various companies and ordered on the internet. However, consumers are rarely aware that normal dwellings are not necessarily suitable places for biodiesel processing, owing to significant quantities of dangerous materials involved in the process and to usually inadequate house environment.

FINAL DISCUSSION

A first and certainly incomplete overview of 1st generation biofuels safety issues arising on their whole life cycle has been proposed, as a contribution of the INERIS BIOSAFUEL project. The typology of risk has been briefly reviewed, at the light of process and side operation flowsheets, as well as at the light of an accident review. Although currently industrialized biofuels, fire safety issues pertaining to the biofuel industry keeps a real issue, and sustainable development of biofuels as a worldwide market will require assistance from western and other experienced countries to implement adequate safety culture in emergent countries, taking account of the many peculiarities that may rely to selected energy crops, and processes. The relatively high number of significant incidents reviewed likely reflects the high mutation in the biofuels market that increases sharply for a number of years, statistically multiplying the number of potential abnormal situations for a given level of risk control. An increasing number of them outlines handling and transportation issues : an emerging risk, recently recognized by specialists in logistics[25].
To our view, in the field of fire safety, research needs cover topics like:
- examination of fire related and other safety issues pertaining to 2nd generation types of biofuels, for which no industrial experience is still available
- follow-up of technical development in the field of valorization of by and co-products of the biofuel industry: a key issue for final cost competitiveness that leads to wide variety of potentially new chemicals derived from glycerin for instance
- data production on: a) combustion species from materials relating to the biofuels industry liable to be involved in accidental fires, including raw materials themselves; b) stability of biofuel characteristics versus time; c) situation of the conventional phys-chem properties of materials currently involved in the biofuel industry according to new regulatory frameworks under implementation due to arrival of REACh and GHS; d) for consolidation of safety measures needed from production to use of E85 in modern fleet; e) consolidation of learning from lessons from past accidents on a word wide basis; f) safety impacts in case of use of biofuels in other transport systems (rail, marine, aircrafts).

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